SIMULATION OF REACTIVE DISTILLATION FOR BIODIESEL PRODUCTION FROM JATROPHA CURCAS SEED OIL

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ABSTRACT

Reactive distillation column (RD column) is a hybrid equipment that combines two of major equipment, i.e. reactor and distillation column. RD column brings many advantages to the chemical industries especially in reducing the cost of building plant, and energy consumption. Biodiesel is an excellent substitute for conventional diesel fuel because of being renewable, nontoxic and biodegradable. In the biodiesel industry, mainly for the biodiesel production from Jatropha Curcas seed oil (JCO oil); the reactive distillation is still being a new technology. The JCO oil contains high percentage of triolein and oleic acid which are really useful for engine performance. This study is mainly based on simulation method by using Aspen Plus 12.1 software. The biodiesel routes process used is triglyceride hydrolysis and fatty acid esterification process. This study will focus on oleic acid esterification with methanol in the reactive distillation column to produce methyl oleate. The simulation was done in equilibrium stage model incorporate with kinetic of reaction model using RADFRAC unit as the RD column model. The purpose of the simulation carried out is to determine the effect of important parameters, i.e. reflux ratio, column pressure, feed temperature, etc, that affect the RD column performance and design the optimized RD column condition to achieve highest product conversion. In the nutshell, the optimum parameters for simulated RD column are; reflux ratio 0.01, feed temperature at 363.15K @ 90^0C, column pressure at 100 kPa, 14 stages with 6 reactive stages, and oleic acid and methanol feed locations, accordingly, at 3^{nd} stage and 8^{th} stage, to achieve 99.65% of oleic acid conversion to biodiesel.

ABSTRAK

Kolum penyulingan bertindakbalas (Kolum RD) adalah satu peralatan gabungan antara dua peralatan yang berbeza cirinya, iaitu rector dan kolum penyulingan. Kolum RD column memberi banyak kelebihan kepada industi kimia terutamanya di dalam mengurangkan kos pembinaan kilang and penggunaan tenaga. Biodiesel adalah pilihan terbaik untuk menggantikan konvensional diesel kerana boleh diperbaharui, tiada toksik and biodegrasi. Di dalam industry biodiesel, terutamanya penghasilan biodiesel daripada minyak mentah dari biji Jatropha Curcas (minyak JCO), Kolum RD masih menjadi teknologi yang baru diperkenalkan. Minyak JCO mempunyai peratusan triolein dan asid oleic yang tinggi dan berguna untuk kemampuan enjin. Kajian ini dijalankan berasaskan kaedah simulasi menggunakan perisian simulasi Aspen Plus versi 12.1. Kaedah pemprosesan biodiesel yang diguankan di dalam kajian ini adalah hidrolisis triglicerin dan pengesteran asid lemak. Kajian ini akn memberi focus kepada pengesteran asid oleic dengan methanol di dalam kolum RD untuk menghasilkan oleate ester. Simulasi telah dijalankan di dalam model keseimbangan bersama dengan model untuk reaksi kinetic menggunakan unit RADFRAC sebagai model kolum RD. Tujuan simulasi ini dijalankan adalah untuk mengenalpasti kesan beberapa parameter yang penting, seperti; nisbah refluk, tekanan kolum, suhu kemasukan bahan mentah, dll, yang memberi kesan kepada kemampuan kolum RD dan merekabentuk kolum RD yang mempunyai keadaan yang optimum untuk mencapai penghasilan produk yang maksimum. Kesimpulannya, optimum parameter untuk simulasi kolum RD adalah; nisbah refluk 0.01, suhu kemasukan bahan mentah pada 363.15K @ 90^0C, tekanan kolum pada 100 kPa, 14 tingkat dengan 6 tingkat reaksi, dan tempat kemasukan asid oleic dan metanol masing-masing pada tingkat 3 dan 8, untuk mecapai 99.65% pertukaran asid oleic kepada biodiesel.

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NOMENCLATURE

cA	-	Oleic acid concentration, mol dm^{-1}
cB	-	Methanol concentration, mol dm^{-1}
cC	-	Methyl Oleate concentration, mol dm^{-1}
cD	-	Water concentration, mol dm^{-1}
$\alpha, \beta, \gamma, \lambda$	-	Reaction order
k	-	Forward rate constant
k’	-	Backward rate constant
A	-	Pre-exponential factor
Ea	-	Activation energy, kJ mol^{-1}
R	-	Rate constant
T	-	Reaction temperature, K

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Demand of fuel and energy sources for daily activities are increasing recently because of the huge development of industries, agriculture, cities, and transportation. However, the fuel from fossil fuel or petroleum today is nearly depleted. Therefore, many researchers from all over the world are seeking alternative sources replacing petrol fuel. One of the solutions is biodiesel.

The usage of vegetable oils in diesel engine could be dated back to the year of 1900 when Rudolf Diesel, the inventor of the engine that bearded his name, demonstrated peanut oil as fuel in Paris World Fair. Their usage continued until 1920's before petroleum derived diesel almost completely eliminated vegetable oils in the market due to cheaper price, higher availability and government subsidies (Li *et al.*, 2010).

However, the altered diesel engine is no longer suitable for high viscosity and low volatility vegetable oils to be applied directly. Refinement has to be made in order to turn those vegetable oils into quality fuel. Several methods have been investigated such as pyrolysis, blending and micro-emulsification to lower the viscosity of vegetable oils (Berchman & Hirata, 2007). Therefore, transesterification process and

esterification process has became the most viable process to transform the vegetable oils to be used in transportation engine.

Nowadays, the new reactive distillation technology has been a major interest to replace the conventional method for biodiesel production. Reactive distillation column is a combination of two major chemical equipments, reactor and distillation column. Thus, in reactive distillation system, the reaction and separation process will be occurring simultaneously. Typically, research has been done on this new technology because of its advantages. A major advantage of reactive distillation is the breakaway azeotropic mixture equilibrium to achieve high conversion of product. (Sahapatsombud et el., 2005)

1.2 PROBLEM STATEMENT

Petroleum product mainly gasoline and diesel have played important role in the world nowadays not only in economics, also in the industrial development. However, it is not a renewable source and contributes to the unwanted effect to the world environment.

Thus, biodiesel are the best replacement for it, which did not cause sulfur contaminant and can be renewed. Although the initial cost to produce is high, the overall cost will be reduced due to a large scale of economies and agricultural subsidies in the future.

Recently, the biodiesel production from various sources especially Jatropha Curcas seed oil is produced using common reactor and distillation system. However, this conventional system in making biodiesel leads to higher cost, maintenance, byproduct production and energy consumption.

Reactive distillation can substitute the conventional reactor and distillation system, which not only potentially reduce the space and cost for equipment and maintenance, but will be able to overcome or breaking the reaction thermodynamic equilibrium (VLE) to obtain higher conversion of desired product.

1.3 OBJECTIVE

a. To develop a reactive distillation model for biodiesel process from Jatropha seed oil.
b. To simulate the reactive distillation model by using Aspen Plus for steady state and dynamic state condition.
c. To determine the optimum parameters (operation and design) to achieve highest conversion of product.

1.4 SCOPE OF STUDY

This research is mainly based on simulation method by using Aspen Plus 12.1 Software. There are three main scopes of research that will be covered to achieve the research objective;

a. Learn and simulate in general for reactive distillation column using Aspen Plus 12.1 Software.
b. Apply the simulation model for common biodiesel data.
c. Validate the simulation model with biodiesel from Jatropha Curcas seed oil experimental data if available.

1.5 SIGNIFICANT OF STUDY

Reactive distillation column is a new technology which could provide more advantages than the conventional reactor and distillation system. A common knowledge in chemical industry is that good equipment leads to high efficiency, produce less unwanted products and energy consumption; which can be found in reactive distillation. This research is intended to improve conventional system for biodiesel production with new development reactive distillation column and to reduce waste and energy consumption which are common issues that biodiesel companies face recently.

CHAPTER 2

LITERATURE REVIEW

2.1 BIODIESEL OVERVIEW

Biodiesel chemically named as fatty acid methyl ester (FAME) and have chemical formula range C_{14}-C_{24} methyl esters. It have been produced from biological sources such as soy bean, palm oil, jatropha, etc; and have chemical and physical properties similar with common diesel fuel.(Kiss, 2009) According to Demirbas, 2009, the biodiesel has boiling point range more than 475K (>202^0C), flash point range about 420K – 450K (147^0C – 177^0C), insoluble in water, and biodegradable.

Recently, biodiesel has attracted worldwide attention to be an alternative fuel sources for replacement of petroleum diesel, which is in the category of non-renewable fuel and will be depleted in limited period of time. (Demirbas, 2009) It also has been a major contribution of air pollution by emission of sulfur oxides, nitrogen oxides, lead, hydrocarbons, etc. By choosing biodiesel an alternative source, not only it renewable, it also free of sulfur, thus making biodiesel a environmental friendly fuel.

Nowadays, the price of biodiesel production is often more expensive than petroleum diesel, but in the future, the price is expected to be reduced due to the agriculture subsidies, and large scale economies. (Kiss, 2009)

2.2 BIODIESEL PRODUCTION

There are many methods to produce biodiesel from various sources. The very basic method is reacting sources with methanol in a batch stirred tank reactor, (Vyas et el., 2009) but recently, there are three methods to produce biodiesel from its sources, oil or fats; that are base catalyzed trans-esterification, solid acid catalyzed esterification and enzymatic catalysis. (Kiss, 2009) From three methods above, the solid acid catalyzed esterification is the most efficient method in biodiesel production because it can operate in a low temperature and pressure environment and yields high conversion with minimal side reaction. (Biodiesel Production, 2007)

Biodiesel from various sources is processed by using common reaction and separation system. There are six systems or processes that currently use at pilot and industrial scale; batch processes using trans-esterification, continuous processes that combine esterification and trans-esterification steps, supercritical processes that required high operating temperature and pressure, hydrolysis and esterification processes that produced high purity of glycerol, enzymatic processes that have low energy consumption, and hydro-pyrolysis processes that required more complex equipment and implies the availability of a low-cost hydrogen course. (Kiss, 2009)

Nowadays, most of the biodiesel processes in industrial scale are using liquid acid or base homogenous catalysts to produce high quality products. However, the uses of homogenous catalyst will lead to major economical and environmental penalties. (Knothe, Gerpen, & Krahl, 2005) Therefore, heterogeneous catalyst (solid acid) was invented to overcome the problems.

2.3 HYDROLYSIS AND ESTERIFICATION PROCESS

For this research, the hydrolysis and esterification process have been taken as the biodiesel production process. In hydrolysis and esterification process plant, there are 2 reactions occurs in the 2 different types of reactors. The first reaction is to hydrolyze triglycerides in the oil feedstock with water to form fatty acid and byproduct, glycerol. The chemical equation for hydrolysis process is stated below;

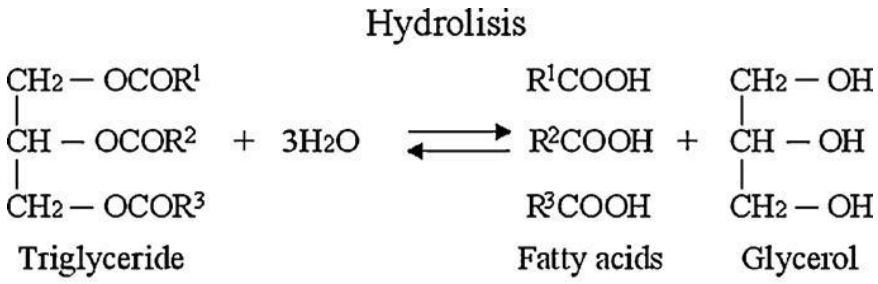

Figure 2.1: Hydrolysis reaction of Triglyceride

Esterification reaction process occurs after the separation of byproduct glycerol form fatty acid in the decanter. The conventional esterification process occurs in the plug flow the reactive distillation column. In esterification reaction, fatty acid will react with methanol with the present of heterogeneous catalyst to form methyl ester (biodiesel) and water as a byproduct. The chemical equation for esterification is stated below;

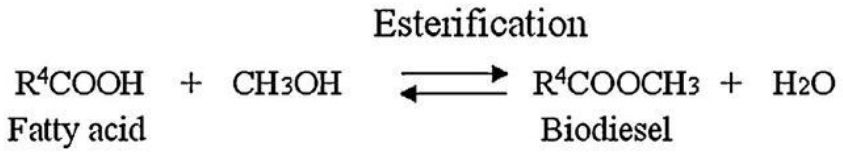

Figure 2.2: Esterification reaction of Fatty Acid

2.4 BIODIESEL PRODUCTION FROM JATROPHA SEED OIL

Jatropha Curcas is a non food plant that grows in arid, semiarid and wasteland. (Lu et el. 2009) This plant has various advantages. Jatropha fruit can be applied to minor wound when it is added with sulfur. Jatropha leaves have anti-malaria properties. The Jatropha roots can treat rheumatism. (For biodiesel production, Jatropha seed can be process to obtain biological oil. From this biological oil, the biodiesel is produce. Jatropha seed oil is categorized as non-edible biological oil sources and has a high-seed yield and high oil content (Wood, 2005).

Recently, the demand for Jatropha oil is increasing tremendously because of the worldwide growing interest for renewable energy sources. (Acten et el., 2008) Plantation of Jatropha plant for biodiesel has become more reasonable rather than other biological source because of the highest amount of biodiesel produce form jatropha plant.

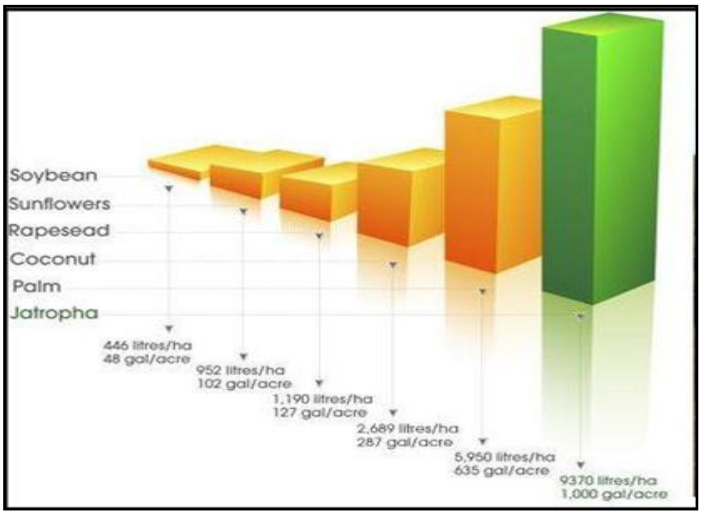

Figure 2.3 Biodiesel production in 1 acre of land for various source (Jatropha Blog, 2009)

Jatropha curcas has been scientifically developed to give better yield and productivity of oil. Jatropha oil has higher cetane number (51) compared to other oils, which is compared to diesel (46–50) and make it an ideal alternative fuel and requires no modification in the engine (Jain *et al.*, 2009). Table 2.1 show the physical n chemical properties for Jatropha Curcas seed crude oil.

From table 2.1, fatty acid compositions in the Jatropha Curcas crude oil have high mass composition of oleic acid (43.1 %) and linoleic acid (34.3%). However, linoleic acid has almost similar physical and chemical properties with oleic acid such as boiling point temperature difference is about 4-5 ^{0}C, and molecular weight different is about 2-3 kg/mol. Therefore, for this simulation study, it is assumed that all the fatty acid composition in the Jatropha Curcas crude oil will consist only oleic acid.

Table 2.1 Physical and chemical properties for Jatropha crude oil taken from http://www.plantoils.in/portal/jatropha/jao/pro/pro.html

PROPERTIES	**VALUE**
Flash point	240/110 °C
Cetane value	51.0
Distillation point (°C)	295 °C
Sulphur %	0.13 %
Viscosity (cp) (30 °C)	52.6 (5.51)2
Speciflc gravity (15 °C/4 °C)	0.917/ 0.923(0.881)
Iodine Value	390.8 -112.5
Acid value	1.0 - 38.2
Palmitic acid %	4.2
Stearic acid %	6.9
Oleic acid %	43.1
Linoleic acid %	34.3
Other acids %	1.4

2.5 ESTERIFICATION KINETIC MODEL

By assumption on the composition in the Jatropha made earlier, for the esterification reaction, only oleic acid will be react with methanol to produce methyl oleate (biodiesel) and water. According to Song et al., 2009, for the esterification of oleic acid and methanol, the reaction rate can be described as:

$$-\frac{dc_A}{dt} = kc_A^{\alpha}c_B^{\beta} - k'c_C^{\gamma}c_D^{\lambda}$$

Figure 2.4 Oleic acid esterification reaction rate (Song et al., 2009)

where c_A, c_B, c_C and c_D denote the concentrations of oleic acid, methanol, methyl oleate and water, respectively; α, β, γ and λ refer to their reaction orders. k and k' are the kinetic constants for the forward and reverse reactions, respectively. However, the value for the rate for reverse reaction is far too small than forward, thus, it assumed neglected.

The rate constants can be used to get the pre-exponential factor, A and activation energy, Ea with the Arrhenius equation,

$$\ln k = -\frac{E_a}{RT} + \ln A$$

Figure 2.5 Arrhenius equation (Song et al., 2009)

Table below shows the values for Arrhenius equation for esterification reaction between oleic acid and methanol using Zinc Acetate catalyst were taken from Song et al., 2009.

Table 2.2. List of parameters and values for rate constant calculation

Parameter	Value
Pre-exponential factor, A	120
Activation energy, Ea	32.62 kJ/mol
Reaction order, n	2.22

2.6 REACTIVE DISTILLATION SIMULATION MODEL

Reactive distillation is a new developed technology for chemical industries especially in biodiesel production. Many researches have been carried out related to this technology to improve the common reactor and distillation system. There are four advantages that make researchers are more interested in studying this new technology, (i) shifting an equilibrium conversion, (ii) improve product selectivity, (iii) breaking azeotropic mixtures, and (iv) saving energy due to the use of reaction heat for separation process (Baur et al., 2000).

One of successful research done by Kiss et el., 2008, making biodiesel suitable to process in reactive distillation column by present of metal oxides catalysts using trans-esterification process. The research is done by using Aspen Plus simulation software. Simulation is an alternative tool to be use in develops or constructs new equipment or technology for new and old process without having risk of lost life, investments, and time to build pilot plant for experiment.

CHAPTER 3

METHODOLOGY

3.1 OVERVIEW

In present study, the simulation was conducted to obtain useful information needed for the design of real plant. Thus, simulation was carried out using Aspen Plus Simulator version 12.1 software package. Radfrac Model with equilibrium stage model is available to be use along this simulation. Moreover, there are kinetic model in the Radfrac system that can be used along the simulation if the required data is available. Before start with any simulation, the base case study simulation is done to ensure the references case for simulation is done within the range. Therefore, in the base case study for the simulation of reactive distillation column, five parameters need to be considered to define all five optimum parameters needed in the design for esterification of oleic acid process; - pressure column, feed temperature, reflux ratio, reactive zone height and feed location.

3.2. ASPEN PLUS 12.1 SOFTWARE

3.2.1 EQULIBRIUM STAGE MODEL

In the simulation of reactive distillation column for esterification of oleic acid with methanol, the chemical reaction equation for esterification process to produce methyl oleate and water is as below;

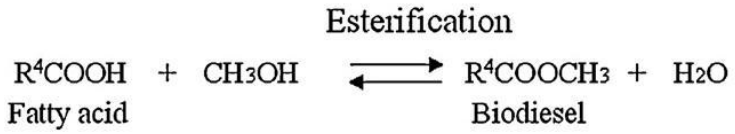

Figure 3.1: Esterification reaction

From previous literature study, there are lack of information on methyl oleate such as vapour pressure and critical temperature. However, all the information ware estimated by the Aspen estimation. For the simulation, the vapour phase was assumed to be ideal and the thermodynamics property method used is UNIQUAC model with the estimation for all missing parameters to represent the concentration coefficient in rate expression.

In the simulation, Radfrac model unit will be use as reactive distillation model. Radfrac model is based on rigorous equilibrium stage model and operate by solving mass balance, energy balance, phase equilibrium, and summation equation. For the Radfrac simulation, assumption of each stage in Radfrac unit is in vapour-liquid equilibrium (VLE) was made.

3.2.2 KINETICS MODEL

In the reaction kinetics model, the key requirement for the simulation to run accordingly to the thermodynamics properties is the accurate reaction kinetics data. In the previous study, the reaction kinetics for oleic acid esterification process was taken from Song et al., 2009. Accordingly, the reaction rate for the esterification of oleic acid and methanol can be described as below;

$$-\frac{dc_A}{dt} = kc_A^{\alpha}c_B^{\beta} - k'c_C^{\gamma}c_D^{\lambda}$$

For the activation energy of esterification reaction between oleic acid and methanol using Zinc Acetate catalyst were taken from Song et al., 2009. The kinetics model will be added in the Aspen Plus Power Law Kinetic Expression.

3.3. BASE CASE STUDY SIMULATION

Base case study simulation has to be done before start with any simulation, as reference data in the simulation to ensure the simulation is run within the base case study range. The flow sheet design for the reactive distillation column equipment process is presented as shown in **Figure 3.2**. The design consist 10 reactive stages from 15 stages used and was characterized by catalyst loading. Oleic acid has high boiling point than methanol. Thus, methanol will be more volatile than oleic acid. Due to that matter, oleic acid is introduced to feed at the top of the column and methanol, on the other hand, will be fed at bottom. By using this feed flows arrangement, the reaction will be occur in counter current ways, which increase effectiveness of reaction. For the molar ratio in the column, both of reactants will fed to the column in 1:1 ratio.